

Hydrothermal treatments of corn cob and hemicelluloses extraction

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Abstract

Corn cob samples were treated with water (autohydrolysis reaction) using a liquid to solid ratio of 10:1 w/w. The optimal condition for extraction of hemicelluloses was found at 185°C for 30 min. This resulted in the release of 9.7% of hemicelluloses (% dry starting material), corresponding to the dissolution of 27.9% of the original hemicellulose. Chemical composition and physico-chemical properties of the samples were elucidated by a combination of sugar analyses and thermal analysis. The results showed that the treatment was effective on the extraction of hemicelluloses from corn cob and that the TGA analysis of xylan from birch wood was found to be initially degraded at about 220 °C whereas hemicelluloses from corn cob would be degraded at about 225 °C.

1 Introduction

Agricultural wastes are mainly of lignocellulosic nature (with cellulose, hemicelluloses and lignin as structural components). Chemically, about 35-55% of the dry material is the glucose polymer cellulose, much of which is in a crystalline structure; while another 25-35% is hemicellulose, an amorphous polymer. The remainder is mostly lignin plus less amounts of minerals, waxes, and other compounds (Sun and Cheng, 2002). Cellulose is formed by $\beta(1-4)$ glucosyl linkages in a linear backbone, whereas hemicelluloses are branched polymers composed of several monosaccharides (Fengel and Wegener, 1989).

Treatments of lignocellulosic materials in autohydrolysis processes (or hydrothermal treatments), under optimized conditions, lead to the solubilisation of hemicelluloses, leaving a solid phase enriched in both cellulose and lignin. These aqueous processes, when used in mild conditions, are an environmentally friendly technology for biomass utilization (Garrote et al., 1999).

On the other hand, corn is the one of the most widely planted crops in the World. According to the Food and Agriculture Organization of the United Nations (FAO, 2008), the annual production worldwide is about 695×10^9 kg. The major production regions are the American continent (53%), Asia (29%), and Europe (11%). In particular, corn cob is an important by-product of this industry: for every 100 kg of corn grain approximately 18 kg of corn cobs are produced (Torre et al., 2008). A large quantity of corn cobs remains unused as lignocellulosic waste or used as animal feed. Owing to their chemical composition, corn cobs show great potential as a renewable raw material for producing a variety of added-value chemicals (Rivas et al., 2004).

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The hemicelluloses fraction of corncobs has a comparatively high content of acetylated xylan (a polymer made up of xylose units with acetyl substituents). When corn cobs are contacted with water and heated, the hydronium ions coming from water autoionisation cause both xylan depolymerisation (sugar oligomers and sugars) and cleavage of acetyl groups (to give acetic acid, which increases the hydronium concentration in the reaction medium) (Garrote, 2002). Autohydrolysis solid residues which contain mainly cellulose and lignin can be subjected to further chemical or biotechnological processing and can also be used as substrate for conversion into a variety of marketable end-products (Parajó et al., 1994).

The aim of this work is to assess the effect of the autohydrolysis treatment of corn cob on the hemicelluloses yield with particular emphasis on the further applications of the extracted fractions.

2 Materials and Methods

Materials

Corn residues (corn cob) were kindly supplied by a local farmer (Portugal). After being dried at 40 °C in an oven for 12 h, the corn cob was cut into small pieces (1-3 cm), milled in a knives' mill to pass through a 0.4 mm screen (for chemical composition) and 1.0 mm (for hydrothermal pre-treatments), and stored at room temperature. All chemicals used were of analytical or reagent grade. Experiments were performed in triplicate and yields are given on a dry weight (untreated corn cob) basis.

Chemical composition of corn cob

Two grams of ground corn cob were treated with 10 mL of 72% H₂SO₄ under stirring at 45 °C for 7 min. The flask was autoclaved for 30 min at 1.05 bar for the complete hydrolysis of oligomers. After filtration through a Sep-Pak C18 cartridge to remove aromatic compounds, the hydrolysate was analyzed in a MetaCarb 67H column at 45 °C using a Shimadzu chromatograph with refractive-index detector. The mobile phase was 0.005 mol/L H₂SO₄ at 0.6 mL/min flow rate. Sugar concentrations, reported as glucan and xylan, were determined from calibration curves obtained with pure compounds. Lignin was determined by gravimetric analysis (Rocha, 2000). All experiments were performed in triplicate.

Hydrothermal treatments

Corn cob samples and water were mixed in a closed and pressurized vessel in order to obtain a liquid/solid ratio of 10:1 w/w, taking into account the moisture content of the sample. The reactor was heated to the desired temperature (165-195 °C) by periods ranging from 10 to 60 min. After each treatment, the liquid phase was separated from the solids by filtration. The hemicelluloses were then precipitated by pouring the concentrated supernatant fluid with three volumes of 95% ethanol (20 °C, 24 h). The precipitates were recovered by filtration, washed with 70 % ethanol and dried (30 °C). All experiments were performed in triplicate.

Thermogravimetric Analyzer

The thermal stability of the samples was evaluated using thermogravimetric analysis (TGA) on a thermal analyzer (TGA-50 Shimadzu, Japan). The apparatus was continually flushed with nitrogen. The samples weighed between 10 and 12 mg and were run from room temperature to 580 °C at a rate of 10 °C/min.

3 Results and Discussion

The compositional data of the corn cob samples used as raw material (average of three replicates) are shown in Table 1. The results are expressed as glucan, hemicelluloses and lignin. Thus, lignocellulosic materials can be defined by their contents of glucan (corresponding to cellulose), xylan (measured as xylose equivalent, which forms the main polymer backbone), xylan substituents (arabinose units, reported as arabinan expressed in sugar equivalent, and acetyl groups), and total lignin (measured as soluble lignin and Klason lignin). As can be seen from Table 1, xylan and xylan substituents (hemicelluloses) accounted jointly for 34.7% of corn cobs (in oven-dried basis).

Samples of corn cob were subjected to hydrothermal treatments in aqueous media under conditions leading to maximal hemicellulose yield. Figure 1 shows that the treatment of corn cob released 0.28 - 9.68 % hemicelluloses (in respect to dry starting material), corresponding to the dissolution of 0.8 and 27.9 % of the original hemicelluloses, respectively. These results revealed that autohydrolysis of the corn cob was effective, and that the highest extraction yield was obtained with 30 min and 185 °C (27.9% of the total available hemicelluloses).

Table 1. Chemical composition of corn cob

Chemical Components	Composition (%)
Glucan	31.8 ± 0.8
Hemicelluloses	34.7 ± 1.1
Xylan	29.4 ± 0.2
Arabinan	1.1 ± 0.2
Acetyl group	3.1 ± 0.4
Total lignin	27.9 ± 0.4
Soluble lignin	11.3 ± 0.2
Klason lignin	16.6 ± 0.4
Total Composition	93.3 ± 0.9

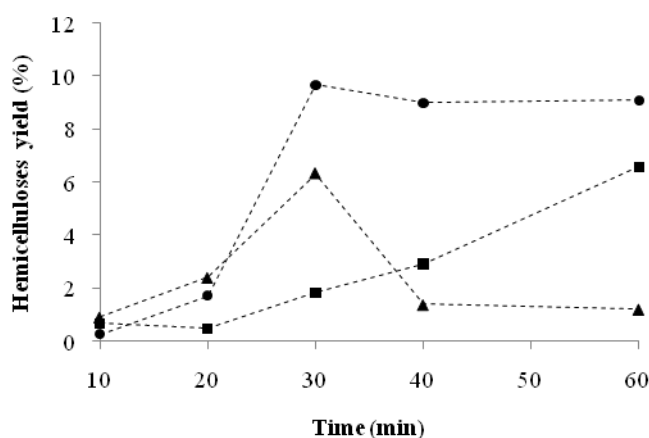


Figure 1. Hemicelluloses yield (%) at temperatures of (■) 165 °C, (●) 185 °C and (▲) 195 °C.

In this work, the thermal properties (Figure 2) of xylan from birch wood (line 1), hemicelluloses from corn cob at 165°C/60 min (line 2), 185°C/30 min (line 3) and 195°C/30 min (line 4) were studied by TGA. Figure 2 and Table 2 show the TGA results obtained of xylan from birch wood and hemicellulose from corn cob. There is distinction between the amounts of the residues remaining after heating of 560 °C heating. All samples have a residual weight between 4.4 and 16.5% at 560 °C (Table 2).

Table 2. Degradation characteristics of the xylan from birch wood, hemicellulose from corn cob at 165°C/60 min, 175°C/40 min, 185°C/30 min and 195°C/30 min.

Samples	Onset of degradation (°C)	Residue after 560 °C (%)
Xylan from birch wood	270	16.5
165 °C/60 min	250	10.9
185 °C/30 min	240	4.4
195 °C/30 min	240	11.9

Samples of xylan from birch wood were found to be initially degraded at about 220 °C whereas hemicelluloses from corn cob at 165°C/60 min, 185°C/30 min and 195°C/30 min would be degraded at about 225 °C. Maximum rates of weight loss were observed between 230 and 320 °C. As observed, samples were stable up to 200 °C. Beyond these temperatures, thermal degradation takes place. As can be seen (Figure 2), for a 30% weight loss, the decomposition temperatures of the degraded samples occurred at 220 °C (lines 2-4) and 280 °C (lines 1). No thermal events were observed at temperatures higher than 560°C.

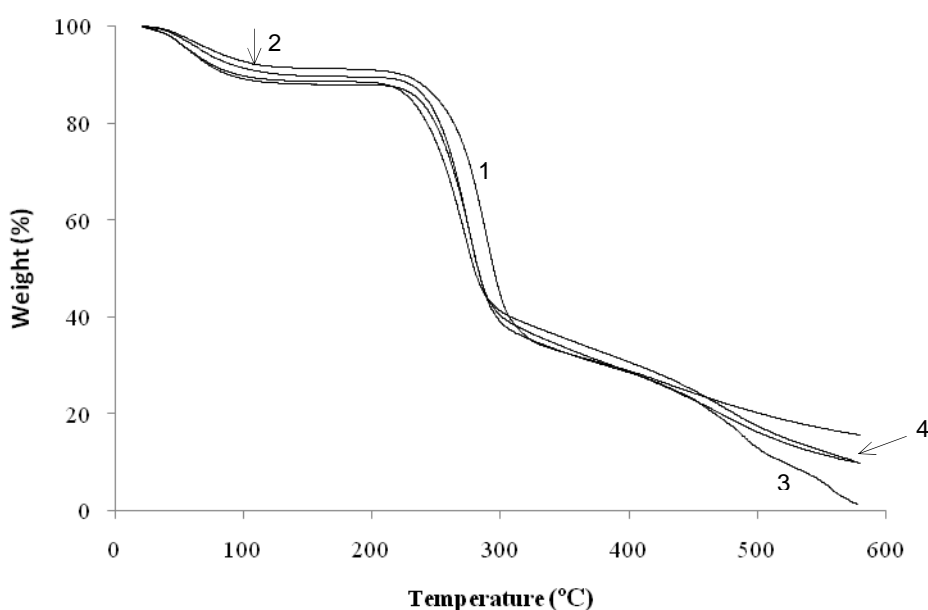


Figure 2. TGA curves of commercial xylan from birch wood (line 1), hemicelluloses from corn cob at 165°C/60 min (line 2), 185°C/30 min (line 3) and 195°C/30 min (line 4).

4 Conclusion

The autohydrolysis treatment of corn cob was effective for the hemicelluloses extraction, and it was shown that the best conditions of extraction were at 185°C and 30 min, obtaining 27.9% of the total available hemicelluloses. Degradation characteristics of hemicellulose (185°C/30min): onset of degradation at 240 °C and residue after 560 °C of 4.4 %.

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